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THEORY OF INTERNAL RELAXATION IN CHEMICAL KINETICS

by

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ABSTRACT

For molecular systems with a relatively small number of degrees
of freedom internal relaxation processes are described by a non-homogeneous
master equation for non-diagonal elements of the density matrix. The
theory is applied to internal vibrational relaxation and intramolecular
rearrangement (isomerization) reactions. The general character and
certain types of solutions of the master equation are investigated.

1) Introduction

In the theory of chemical reactions the reaction pro-
cess is often pictured as the consequence of two interfe-
ring mechanisms which may be named external and internal
collisions. Sometimes one also refers to the latter mecha-
nism as "redistribution of energy between different degrees
of freedom". In many instances, as in the case of unimole-
cular reactions and of bimolecular reactions with long-li-
ving reaction complexes, it is the internal mechanism
which plays the decisive role in transferring a molecule
or supermolecule from one region of relative stability
within the configuration space to another. The perturbation
by the external collisions of a molecular system can then
be assumed to remain localized within one of its chemical
configurations, with other words, reaction in such cases
is very unlikely to occur as the immediate consequence of
an external collision.

Picturing the reaction by the internal mechanism was
extremely fruitful in the theory of unimolecular reactions[1,2,3]

[1] O. K. Rice, H. C. Ramsperger, J. Am. Chem. Soc.
49, 1617 (1927), 50, 617 (1928)
R. A. Marcus, O. K. Rice, J. Phys. Chem.
55, 894 (1951)
[2] L. S. Kassel, J. Phys. Chem. 32, 225 (1928)
[3] N. B. Slater, Theory of Unimolecular Reactions
Cornell, Ithaca, New York, 1959, p 22.

and we shall refer to it explicitly throughout this paper.
One of the assumptions, used in specifying the internal

mechanism, is that the reactant molecules with internal
energy E_i form a microcanonical ensemble with equilibrium
properties (i.e., constant density in phase space over
the reactant region of the energy shell $E_i...E_i + dE_i$,resp.
commutativity of the density matrix with the Hamiltonian
of the reactant-species). This implies the existence of
an intramolecular relaxation process with a relaxation
time short compared with the time between the external
collisions. Since molecules have a very small number of
degrees of freedom it is not at all evident whether and
under which circumstances such internal relaxation mecha-
nisms may be taken as granted. The reaction process itself
also needs further clarification. Particularly in the case
of an intramolecular rearrangement reaction (also termed
"isomerization reaction") one again makes explicit use
of the assumption that there is an intramolecular relax-
ation mechanism, since otherwise the molecule would remain
oscillating between reactant and product configuration till
the external collisions had damped these oscillations away.
In the latter case, however, a first order rate process
could never be observed.

From the viewpoint of statistical mechanics the pro-
blem of intramolecular rearrangement reactions is the more
intriguing one since all energy levels of the reacting mo-
lecule are discrete and non-degenerate. The forthcoming
treatment can easily be specialized to monomolecular de-
composition reactions. It also contains the special case
of internal vibrational relaxation.

To the knowledge of the author, the only treatment,
of intramolecular rearrangements, different from the scheme
used for monomolecular dissociation reactions was given by
Golden and Peiser[4] who based their approach on the repeated
random phases assumption. S. Golden[5] also focussed attention

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4) S. Golden, A.M. Peiser, J. Phys. and Coll.Chem., 55, 789 (1951)
5) S. Golden, Suppl. Nuovo Cimento, 5, 540 (1957), 15,335 (1960)
and private communication

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on the problem of how to understand the intuitive concept
of chemical species in terms of quantum mechanics which is
of prime importance for the present case.

Intramolecular rearrangement reactions represent a problem
by its own nature in statistical mechanics. The systems we are
dealing with have a comparatively small number of degrees of
freedom so that some of the assumptions, generally agreed on,
for the derivation of a master equation do not hold. Furthermore,
in contrast to the main goal of the statistical mechanical treat-
ment of ordinary systems, except those with magnetic fields,
where one calculates the time dependence of the diagonal elements
of the density matrix, we are exclusively interested in the
non-diagonal elements of $\varrho(t)$. The master eqation we are to
derive will be non-homogeneous (reflecting the fact that the
initial density matrix does not commute with the unperturbed
Hamiltonian $\mathcal{H}_o$) and the solution at very large times will
shape into a diagonal density matrix. The relaxation times
for the non-diagonal matrix elements to disappear can then be
related to internal vibrational relaxation and the rate of
intramolecular chemical change. Rates of reactions calculated
on the basis of a purely internal relaxation mechanism, will be
meaningful as long as the relaxation time of the unperturbed
system under the action of outer collisions is long compared
with the time for relaxation by the internal perturbation.

2) Characterizing Reactant- and Product Species in a System with Intramolecular Change

The concept of molecular species, as it is used in chemistry, has no correspondence in basic theories for the description of nature, like classical mechanics and quantum mechanics. The reason is that the chemical aspect of matter is an operational one which can be characterized by certain limited sets of measurements. Other properties of matter are considered to be beyond the scope of chemistry.

S. Golden[5] has given a comprehensive formal description of the operational structure of chemistry postulating the existence of complete sets of commuting observables which can be used to determine the chemical state of matter in accordance with the intuitive traditional concept of chemical species. For the purpose of the present investigation the construction of such a set of commuting observables will be instrumental. At the same time the limitations of the chemical viewpoint for molecular species which can convert into each other will become obvious.

In dealing with a certain class of chemical reactions, as a first step we have to characterize the properties of any set of measurements suitable for distinguishing between the different molecular species and for further determination of the chemical situation. Out of the wide range of chemically relevant measurements there may be selected different sets with commuting observables comprising only the minimal number of measurements necessary for complete determination of the chemical state of a system. Each such set can be divided into two parts so that it will contain measurements which serve the purpose to distinguish between different chemical species (e. g. molecules M_1, M_2, ... or clusters of

molecules M_1M_1, M_1M_2, ..., $M_1M_1M_1$, $M_1M_1M_2$, ... etc.) and also measurements which will complete the quantum mechanical information, so that an initial density matrix ρ_o is uniquely determined.

Any two chemically relevant measurements must enable us to distinguish between atleast two chemical species. Now from physical insight it is known that chemical species may always be characterized by the atoms (or ions) out of which they can be thought to be built up, furthermore by their "chemical structure" which usually refers to a certain range for the relative positions of the nuclei. "Chemical structure", however, may also be understood in a broader sense, comprising electrons localized with respect to some of the nuclei, thus allowing ions or even local excitations to appear as a chemical species. We may idealize any set of measurements for determining chemical structure by a single observable "configuration", denoted by $\mathcal{K}$. For our purposes it is not necessary to introduce measurements of the elementary composition (numbers of electrons and atomic nuclei) explicitely.

In the case of an intramolecular rearrangement $\mathcal{K}$ will not even approximately commute with the Hamiltonian $\mathcal{H}$, nor will it commute with $\mathcal{H}_o$, since energy and local coordinates do not commute. Nevertheless, there must be an observable related to the energy of a molecule in one of its chemical configurations. Let us assume there are only two chemical species involved, the configuration of which can be found by measuring $\mathcal{K}^I$ and $\mathcal{K}^{II}$.

$$tr\left(\mathcal{K}^{I}\rho\right) = \frac{N_I}{N} \quad \text{and} \quad tr\left(\mathcal{K}^{II}\rho\right) = \frac{N_{II}}{N} \quad,$$

where tr denotes the trace of a matrix, will then be the relative numbers of molecules in configurations I and II respectively and the initial density will commute with $\mathcal{K}^{I}$:

$$[\mathcal{K}^{I}, \rho_o] = 0$$

The Hamiltonian and also the unperturbed Hamiltonian must now be divisible into the following parts

$$\mathcal{H}_o = \mathcal{H}_o^{I} + \mathcal{H}_o^{II} + \mathcal{H}_o^{I,II}$$

$$\mathcal{H} = \mathcal{H}^{I} + \mathcal{H}^{II} + \mathcal{H}^{I,II}$$

where

$$[\mathcal{H}_o^{I}, \mathcal{K}^{I}] = 0 \quad, \quad [\mathcal{H}^{I}, \mathcal{K}^{I}] = 0$$

and

$$[\mathcal{H}_o^{II}, \mathcal{K}^{II}] = 0 \quad, \quad [\mathcal{H}^{II}, \mathcal{K}^{II}] = 0$$

$\mathcal{H}^{I}$ and $\mathcal{H}^{II}$ are representing the non-reacting species I and II. The bound eigenfunctions of $\mathcal{H}^{I}$ and $\mathcal{H}^{II}$, also of $\mathcal{H}_o^{I}$ and $\mathcal{H}_o^{II}$, must then be localized in the regions of the respective chemical configurations. Thus, the eigenfunctions $|\alpha_I'\rangle$, $|\alpha_{II}'\rangle$ and $|\alpha_I\rangle$, $|\alpha_{II}\rangle$, satisfying

$$\mathcal{H}^{I}|\alpha_I'\rangle = E_\alpha^{I'}|\alpha_I'\rangle \qquad \mathcal{H}^{II}|\alpha_{II}'\rangle = E_\alpha^{II'}|\alpha_{II}'\rangle$$

and

$$\mathcal{H}_o^{I}|\alpha_I\rangle = E_\alpha^{I}|\alpha_I\rangle \qquad \mathcal{H}_o^{II}|\alpha_{II}\rangle = E_\alpha^{II}|\alpha_{II}\rangle$$

will be eigenfunctions of $\mathcal{K}^{I}$ and $\mathcal{K}^{II}$, with

$$\mathcal{K}^{I}|\alpha_I'\rangle = |\alpha_I'\rangle$$

$$\mathcal{K}^{I}|\alpha_{II}'\rangle = 0$$

$$\mathcal{K}^{I}|\alpha_I\rangle = |\alpha_I\rangle \qquad \text{and similar equations for II.}$$

$$\mathcal{K}^{I}|\alpha_{II}\rangle = 0$$

If $\left\{|\alpha_I'\rangle, |\alpha_{II}'\rangle\right\}$ and also $\left\{|\alpha_I\rangle, |\alpha_{II}\rangle\right\}$ span the whole Hilbert

space $\mathcal{K}^I$ and $\mathcal{K}^{II}$ are projection operators. Moreover, since $|\alpha_I\rangle$ and $|\alpha_{II}\rangle$ are so strongly localized in the region of configuration I or II respectively, one configuration operator will be the orthogonal complement of the other. Thus

$$\mathcal{K}^I = 1 - \mathcal{K}^{II}$$

and

$$tr(\mathcal{K}^I \rho) + tr(\mathcal{K}^{II}\rho) = 1$$

Explicit constructions of $\mathcal{H}_o^I$, $\mathcal{H}_o^{II}$, $\mathcal{K}^I$ and $\mathcal{K}^{II}$ will be given in chpt. 3.

At the initial time t=0 an ensemble of molecules shall exist as chemical species I, i.e it is represented by a density matrix ρ which is diagonal in the eigenrepresentation of $\mathcal{K}^I$ and $\mathcal{H}_o^I$,

$$\rho_o = \sum_{\alpha_I} |\alpha_I\rangle P_\alpha^I \langle\alpha_I| .$$

This initial density will now decay in two ways:

1) leakage through the barrier between configuration I and II by tunnel -effect

and

2) transitions caused by the perturbation $\mathcal{V}$.

A characteristic time, denoted by τ_l and τ_r , can be related to both of these processes. The time τ_m, available for the measurement of $\mathcal{K}^I$ and $\mathcal{H}_o^I$, is therefore limited by τ_l and τ_r . To be sure that our ensemble has not changed considerably during the measurement we have to make $\tau_m \ll min(\tau_l, \tau_r)$

A limited time for the measurement of $\mathcal{K}^I$ and $\mathcal{H}_o^I$ implies an uncertainity in the energy of the order τ_m^{-1} . On the other hand, if ρ_o decays very rapidly by tunnel-effect and transitions, τ_m^{-1} may become so large that the measurement of $\mathcal{H}_o^I$ would spread out the energy of the ensemble way

above the barrier between configurations I and II. We shall exclude this interesting case here since it is beyond the scope of chemical kinetics, assuming $\tau_m^{-1} \ll E_{at}$)

where E_{at} is an energy of the order of the height of the barrier between regions I and II.

For nearly all chemical systems one can replace $\mathcal{H}_o^I$ by two dependent measurements, $\mathcal{E}^I$ and $\mathcal{D}_e^I$, $\mathcal{E}^I$ representing the electronic state of the system, its eigenvalues e labelling sets of electronic quantum numbers, whereas $\mathcal{D}_e^I$ denotes the observable related to the vibronic energy attributed to the electronic state e. $\mathcal{E}^I$ and $\mathcal{D}_e^I$ commute for at least most systems of chemical interest. More frequently, however, we shall find that $\mathcal{E}$ and $\mathcal{D}_e$, the corresponding operators for the whole system, do not commute. Then Born-Oppenheimer separation does not hold and the ensemble of reactant molecules will change its distribution over the electronic states in the course of the reaction. Commuting operators, related to $\mathcal{E}$ and $\mathcal{D}_e$, can nearly always be constructed in the following way. Denoting all electronic coordinates by x, all nuclear coordinates by X and letting $\widetilde{T}_K$ and $\widetilde{T}_{el}$ represent the kinetic energy operators of nuclei and electrons respectively, the total hamiltonian is (in the absence of magnetic forces)

$$\mathcal{H} = \widetilde{T}_K + \widetilde{T}_{el} + \mathcal{U}(x,X)$$

Solving

$$\{ \widetilde{T}_{el} + \mathcal{U}(X,x) \} |e\rangle = E_e |e\rangle$$

we can define

$$\mathcal{E} = \sum_e |e\rangle e \langle e|$$

and

$$\mathcal{D}_e = \langle e| \mathcal{H} |e\rangle$$

The diagonal part of the operator $\mathcal{D}_e$, given by

$$\mathcal{D}_e^{(\alpha)} = \sum_e |e\rangle\langle e| \mathcal{H} |e\rangle\langle e|$$

will then commute with $\mathcal{E}$. By this method we can always construct sets of commuting operators, like

$$\mathcal{H}^{I}, \, \mathcal{E}^{I}, \, \mathcal{D}_1^{I(\alpha)}, \, \mathcal{D}_2^{I(\alpha)}, \cdots$$
$$\mathcal{H}^{II}, \, \mathcal{E}^{II}, \, \mathcal{D}_1^{II(\alpha)}, \, \mathcal{D}_2^{II(\alpha)}, \cdots$$

It is clear that in cases like the above mentioned the non-diagonal part of $\mathcal{D}_e$ would occur as part of the perturbation operator $\mathcal{V}$ on a later stage of the theoretical treatment.

3) Quantum Theory of Internal Motion of a Molecule

Description of the reaction process requires the construction of a special set of eigenfunctions for the internal motion of a molecule[6]. To this end we shall make

[6] see L. Hofacker, Z. Naturforsch. 18 a, 607 (1963)

two restrictive assumptions:

1) The whole reaction takes place under a fixed set e of electronic quantum numbers. $\mathcal{E}$ will therefore commute with $\mathcal{H}$, $\mathcal{D}$ and $\mathcal{D}_e^{(d)}$.

2) Only the action of conservative forces is taken into account. Hence, Coriolis forces will be neglected after introducing a coordinate system which moves and rotates with the molecule.

If there are N atomic nuclei with coordinates $X_1, \ldots, X_{3N}$ in a coordinate system, rigidly fixed to the molecule, the forces acting on them will have a potential

$$U_{J\tau}(X_1, \ldots, X_{3N})$$

which contains the centrifugal forces and depends therefore on the rotational quantum numbers J and τ (related to total angular momentum and one of its components).

The inner motion of the molecule is now represented by wave packets moving on the potential energy surface . The potential has the shape of two double moulds and the process of innermolecular conversion takes place by the passage of wavepackets from one mould to the other. Solutions for the motion of waves in all regions of the many-dimensional potential energy surface are, of course, extremely difficult to obtain. However, since the wave packets represent thermal energy, their statistical

weights become lower and lower as their energy
rises. Examining the problem from this angle we may say
that the rate of the reaction will be determined by those
wave packets which pass the saddle between the two moulds
near its lowest point having little kinetic energy at the
same time. Those wave-packets will follow rather closely
a line of minimum curvature, termed the "reaction path",
which leads from the bottom of one mould across the saddle
point to the other mould.

Our concern now has to be a twofold one. In the first
place we want to calculate the flux of wave-packets along
the reaction path. This implies to establish a complete
system with the property to factorize the motion along the
reaction path from motion in other directions. On the other
hand, we shall try to exploit the fact that the deviation
of the center of wave packets from the reaction path is small.

First we determine a family of coordinate surfaces

$$\eta_2 = \eta_2(X_1, \ldots, X_{3N})$$
$$\vdots$$
$$\eta_M = \eta_M(X_1, \ldots, X_{3N})$$

(5)

(there are M internal
degrees of freedom)

which shall have the property to contain the reaction path
so that

(6) $$\eta_2 = \eta_3 = \cdots = \eta_M = 0$$

is a set of equations which has the point-set of the reaction
path as its only solution. The coordinate surfaces $\eta_i = const.$
will then intersect with the reaction path.

In the system of skewed internal coordinates the kinetic energy operator is

$$(7) \qquad T = \frac{1}{2} G^{1/2} \sum_{ij=1}^{M} \frac{\partial}{\partial \eta_i} G^{-1/2} G^{ij} \frac{\partial}{\partial \eta_j} = \sum_{ij=1}^{M} T^{ij}$$

(8a) where

$$G^{ij} = \sum_{\ell=1}^{3N} \frac{1}{m_\ell} \frac{\partial \eta_i}{\partial X_\ell} \frac{\partial \eta_j}{\partial X_\ell}$$

(8b) and

$$G = \det G^{ij}$$

We shall, from now on, distinguish the coordinate η_1 by denoting it as ξ. It is our aim to find a complete system which separates ξ from the other coordinates. This can, in general, not be obtained, yet, it is possible to find a complete set for the internal nuclear motion of the molecule where the eigenfunctions have the form:

$$(9) \qquad \Psi(\xi, \eta_2, \ldots, \eta_M) = \Phi(\xi) \varphi(\xi, \eta_2, \ldots, \eta_M)$$

with the property that

$\Phi(\xi)$ behaves wave-like in ξ

$\varphi(\xi, \eta_2, \ldots, \eta_M)$ is a wave-type function in $\eta_2, \ldots, \eta_M$ but __not__ in ξ; the variation in ξ will befound to depend on certain curvatures of the potential energy surface.

If we determine

$$\xi = \eta_1 (X_1, \ldots, X_{3N})$$

such that

$$(10) \qquad G^{12} = G^{13} = \cdots = G^{1M} = 0$$

the kinetic energy operator now reads

$$(11) \qquad T = T^{11} + \sum_{i,j=2}^{M} T^{ij}$$

$$= T^\xi + T^\upsilon$$

The Hamiltonian is

$$\mathcal{H} = \mathcal{T} + \mathcal{U}$$

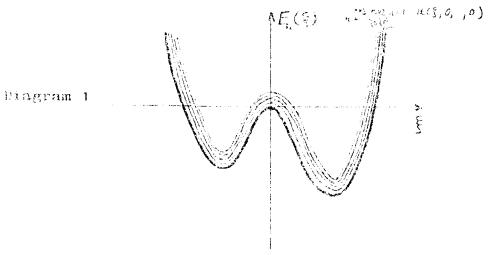(12)
$$= \mathcal{T}^{\xi} + \mathcal{T}^{v} + \mathcal{U}$$

$$= \mathcal{T}^{\xi} + \mathcal{H}^{v}$$

Note that $\mathcal{T}^{\xi}$ depends on all internal coordinates but contains only differentiations with respect to ξ whereas $\mathcal{H}^{v}$ depends on ξ only as a parameter.

Then the eigenvalue problem

(13)
$$\mathcal{H}^{v}|n\rangle = E_n(\xi)|n\rangle$$

produces $E_n(\xi)$ curves of the following kind

Diagram 1

These curves do not intersect by reasons similar to those found for spectroscopic terms. Furthermore, we may define the diagonal part of the operator $\mathcal{T}^{\xi}$ with respect to $\{|n\rangle\}$:

(14)
$$\mathcal{T}^{\xi}_{(d)} = \sum_n |n\rangle\langle n| \, \mathcal{T}^{\xi} \, |n\rangle\langle n|$$

and solve the eigenvalue problem

(15)
$$\left\{\langle n| \, \mathcal{T}^{\xi} \, |n\rangle + E_n(\xi)\right\}|\widetilde{n\nu}\rangle = E_{n\nu}|\widetilde{n\nu}\rangle$$

where $|\widetilde{n\nu}\rangle$ depends on ξ only. Then it is easy to see that

(16) $$|n\nu\rangle = |n\rangle|\widetilde{n\nu}\rangle$$

is an eigenfunction for

(17) $$\left\{ T_{(d)}^{\xi} + \mathcal{H}^{\nu} \right\}|n\nu\rangle = E_{n\nu}|n\nu\rangle$$

We write this equation in the form

(18) $$\mathcal{H}_0 |n\nu\rangle = E_{n\nu}|n\nu\rangle$$

Since the non-diagonal part of T^{ξ}, $T_{(nd)}^{\xi}$ is defined by

(19) $$T^{\xi} = T_{(d)}^{\xi} + T_{(nd)}^{\xi}$$

the Hamiltonian is now split up into a main part and a perturbation $\mathcal{V}$:

(20)
$$\mathcal{H} = \mathcal{H}_0 + T_{(nd)}^{\xi}$$
$$= \mathcal{H}_0 + \mathcal{V}$$

Assuming that wave-packets which lead to reaction will not deviate much from the reaction path we may expand the potential in eq.(13) to second order terms in the η_k and use familiar methods for the treatment of small vibrations. In the vicinity of a point on the reaction path with coordinate ξ the coordinate surfaces η_k = const may be substituted by their tangential planes,

(21a) $$\eta_k = c_{k0}(\xi) + \sum_{\ell=1}^{3N} c_{k\ell}(\xi) x_\ell$$

or in matrix notation

(22b) $$\eta = c_0 + \mathbf{C} x$$

After any initial choice of the coordinate surfaces η_k in this approximation all G^{ik} for $i, k \geqslant 2$ become functions of ξ only, hence

$$(23) \qquad \mathcal{J}^{\nu} = \frac{1}{2} \sum_{i,k=2}^{M} G^{ik} \frac{\partial}{\partial \eta_i} \frac{\partial}{\partial \eta_k}$$

Expansion of the potential yields

$$(24) \qquad \mathcal{U}(\xi, \eta_1, \cdots, \eta_M) = \mathcal{U}(\xi, 0, \cdots, 0) + \sum_{i=2}^{M} f_i(\xi)\eta_i + \sum_{i,k=2}^{M} \frac{1}{2} k_{ik}(\xi)\eta_i \eta_k$$

The $f_i(\xi)$ will in general not be zero wherefore we introduce new coordinates

$$(25) \qquad \overline{\eta}_i = \eta_i - a_i(\xi) \qquad \text{or} \qquad \overline{\eta} = \eta - a$$

thus that

$$(26) \qquad \overline{\mathcal{U}}(\xi, \overline{\eta}_1, \cdots, \overline{\eta}_M) = \overline{\mathcal{U}}(\xi, 0, \cdots, 0) + \sum_{i,k=2}^{M} \frac{1}{2} k_{ik}(\xi)\overline{\eta}_i \overline{\eta}_k$$

and

$$(27) \qquad \mathcal{H}^{\nu} = \frac{1}{2} \sum_{i,k=2}^{M} G^{ik}(\xi) \frac{\partial}{\partial \eta_i} \frac{\partial}{\partial \eta_k} + \overline{\mathcal{U}}(\xi, 0, \cdots, 0) + \sum_{i,k=2}^{M} \frac{1}{2} k_{ik}(\xi)\eta_i \eta_k$$

Now a new reaction path which may be called the "dynamic reaction path" can be defined by the set of equations (cf. equs.(6))

$$(28) \qquad \overline{\eta}_2 = \overline{\eta}_3 = \cdots = \overline{\eta}_M = 0$$

Since all this holds for a fixed ξ we have to put

$$(29) \qquad \overline{\xi} = \xi$$

In equ. (27) kinetic and potential energy can be made a sum of square terms by a transformation

$$(30) \qquad \overline{\eta} = A \tilde{\eta} \quad , \quad \tilde{\eta} = \begin{pmatrix} \tilde{\eta}_2 \\ \vdots \\ \tilde{\eta}_M \end{pmatrix} .$$

so that it now reads

(31)
$$\mathcal{H}^{\nu} = \frac{1}{2} \sum_{i=2}^{M} \left\{ G_i(\xi) \frac{\partial^2}{\partial \widetilde{\eta}_i^2} + k_i(\xi) \widetilde{\eta}_i^2 \right\} + \bar{\mathcal{U}}(\xi, 0, \cdots, 0)$$

It can be shown that in the new coordinate system equs.(10) still hold.

From (22b) and (25) follows

$$\bar{\eta} - c_0 - a + \mathbb{C}x$$
$$= \bar{\mathbb{C}}_0 + \mathbb{C}x , \qquad\qquad \bar{c}_0 = c_0 - a ,$$

and with (30) we have

$$\mathbb{A}\widetilde{\eta} - c_0 + \mathbb{C}x$$
$$\widetilde{\eta} = \mathbb{A}^{-1}c_0 + \mathbb{A}^{-1}\mathbb{C}x$$
$$= \widetilde{c}_0 + \widetilde{\mathbb{C}}x ;$$

(32)
$$\widetilde{c}_0 = \mathbb{A}^{-1}\bar{c}_0$$
$$\widetilde{\mathbb{C}} = \mathbb{A}^{-1}\mathbb{C}$$

Starting with(32) instead of (22) equs.(10) become

$$G^{1k} = \sum_{\ell=1}^{3N} \frac{1}{m_\ell} \frac{\partial \xi}{\partial x_\ell} \frac{\partial \eta_k}{\partial x_\ell}$$
$$= \sum_{\ell=1}^{3N} \frac{1}{m_\ell} \frac{\partial \xi}{\partial x_\ell} \widetilde{c}_{k\ell}(\bar{\xi})$$
$$= 0 \qquad\qquad (k = 2, 3, \cdots, M)$$

or
(33)
$$\widetilde{\mathbb{C}} \widetilde{\alpha} = 0 \qquad\qquad \text{where} \qquad \widetilde{\alpha}_\ell = \frac{1}{m_\ell}\left(\frac{\partial \xi}{\partial x_\ell}\right) , \qquad \widetilde{\alpha} = \begin{pmatrix} \widetilde{\alpha}_1 \\ \vdots \\ \widetilde{\alpha}_{3N} \end{pmatrix}$$

On the other hand, the particular form of the Hamiltonian
we are making use of was attained by choosing some $\mathcal{A}$
which satisfies, according to (22), the equation

(34) $$\mathbb{C}\,\mathcal{A} = 0$$

Since $\mathbb{A}$ is non-singular, (33) is fullfilled by putting

(35) $$\widetilde{\mathcal{A}} = \mathcal{A}$$

We can therefore, in the limit of small oscillations around
the reaction path, change the η -coordinates to the $\tilde{\eta}$
without violating the condition (10).

After all, we can write the energy $E_n(\xi)$ in a more
elaborate form

(36) $$E_n(\xi) = \sum_{i=2}^{M} \omega_i(\xi)(n_i + \tfrac{1}{2}) + \overline{\mathcal{U}}(\xi, 0, \cdots, 0)$$

By this approach we have neglected all anharmonicities
except those which occur along the reaction path. Undoubtedly,
in chemical reactions the anharmonicities a wave-packet
is subject to on its way streight towards the saddle will
in general be more important than those of oscillatory
motions which can not immedicately lead to reaction.

We finally have to give a proper definition of the
one-mould Hamiltonians $\mathcal{H}_0^{\mathcal{I}}$ and $\mathcal{H}_0^{\mathcal{I}}$ which one needed to
construct the initial density matrix ρ_0 . From equ. (13)
follows the set of curves $E_n(\xi)$. Let us denote the maximum
in the middle of the n-th curve by ξ_n , then we may define

$$\mathcal{H}^v(\xi)|n\rangle = \mathcal{H}^{Iv}(\xi)|n_I\rangle = E_n^I(\xi)|n_I\rangle \qquad \text{for} \quad \xi < \xi_n$$

$$\mathcal{H}^v(\xi)|n\rangle = \mathcal{H}^{IIv}(\xi)|n_{II}\rangle = E_n^{II}(\xi)|n_{II}\rangle \qquad \text{''} \quad \xi > \xi_n$$

$|n_I\rangle$ and $|n_{II}\rangle$ will then be equal to $|n\rangle$ in their respective regions. Furthermore, choosing $E_n^I(\xi) = E_n^I(\xi_n)$ for $\xi \geqslant \xi_n$, we may define $|\widetilde{n\nu_I}\rangle$ and $E_{n\nu}^I$ by

$$\left\{ \langle n_I | T^\xi | n_I \rangle - E_n^I(\xi) \right\} |\widetilde{n\nu_I}\rangle = E_{n\nu}^I |\widetilde{n\nu_I}\rangle$$

with a similar equation holding for mould II.

Thus $\mathcal{H}_o^I$ and $\mathcal{H}_o^{II}$ are given eigenfunctions and eigenvalues $|n_I\rangle|\widetilde{n\nu_I}\rangle$, $E_{n\nu}^I$ and $|n_{II}\rangle|\widetilde{n\nu_{II}}\rangle$, $E_{n\nu}^{II}$ respectively. it shall be noted here that for the problem we are investigating only bound eigenfunctions, located in mould I or II, are of any interest.

$\mathcal{K}^I$ and $\mathcal{K}^{II}$ can then be defined by

$$\mathcal{K}^I = \sum_{\substack{n\nu_I \\ \text{(bound states)}}} |n\nu_I\rangle\langle n\nu_I| \quad , \qquad \mathcal{K}^{II} = \sum_{\substack{n\nu_{II} \\ \text{(bound states)}}} |n\nu_{II}\rangle\langle n\nu_{II}| .$$

4) Derivation of Relaxation Equation.

We shall now consider an isolated molecule with an
initial density ρ_0 which is non-diagonal in the eigenstates
of the total Hamiltonian $\mathcal{H}$. The crucial question is what
the asymptotic behaviour in time of such a system might be.
Molecules are finite systems and therefore it is not evident
whether we shall be able to derive a master-equation
describing the internal relaxation process. It can easily
be recognized that not all the assumptions employed for
infinite systems by van Hove and others[7,8,9] in order

7) L. van Hove, Physica 21, 517 (1955); 23, 441 (1957);
25, 268 (1959)

8) R.W. Zwanzig, Lectures in Theoretical Physics III, Boulder
1960, Interscience, New York, 1961, p. 106

9) A. Janner, Helv. Phys. Acta 35, 47 (1962); 36, 857 (1963)

to derive a master equation will hold. Nevertheless, we
shall be able to establish an asymptotic solution of the
von Neumann-equation which holds on a certain time scale.
This can be done in a more straightforward way by direct
investigation of the damping form of von Neumann's equation
than by applying a Laplace-transform method[10,11,12,13].

10) W. Kohn, J.M. Luttinger, Phys. Rev. 108, 590 (1957)

11) S. Nakajima, Progr. Theor. Phys. (Kyoto), 20, 948 (1958)

12a) E.W. Montroll, Lectures in Theoretical Physics, III, Boulder
1960, Interscience, New York, 1961, p. 221

12b) E.W. Montroll, Fundamental Problems in Statistical Mechanics
Nijenrode Castle 1961, North Holland,
Amsterdam (subsequently cited as: Nijenrode
1961) p. 230

13). J. Hajdu, Can. J. Phys. 41, 533 (1963).

In applying the results to intramolecular rearrange-
ments we shall make use of ideas, essential in all common
theories of monomolecular reactions [3], saying that under
certain conditions the effect of collision with a heat-bath
will be neglegible.

Deriving the damping-form of von Neumann's equation we
may follow the well-known procedure, yet keep in mind that
ρ_0 will not commute with the hamiltonian of the unper-
turbed system, $\mathcal{H}_0$. Let the perturbation be the hermitien
operator V which may be identical with $\widetilde{H}_{(n)}$ in chpt. 3. How-
ever, V and $\mathcal{H}_0$ in principle may also comprise electronic
terms. The Hamiltonian $\mathcal{H}$ of the molecule will then be

$$\mathcal{H} = \mathcal{H}_0 + V$$

and von Neumann's equation is

$$(37) \qquad i\dot{\rho} = [\mathcal{H}, \rho]$$

Defining
$$\bar{\rho}(t) = e^{i\mathcal{H}_0 t}\rho(t)e^{-i\mathcal{H}_0 t}$$

we find by differentiation
$$\dot{\bar{\rho}}(t) = -i\,e^{-i\mathcal{H}_0 t}[V,\rho]\,e^{i\mathcal{H}_0 t}$$

and by integration

$$\bar{\rho}(t) - \rho_0 = -i\int_0^t e^{-i\mathcal{H}_0 \tau}[V,\rho(\tau)]\,e^{i\mathcal{H}_0 \tau}\,d\tau$$

or

$$\rho(t) = e^{-i\mathcal{H}_0 t}\rho_0\,e^{i\mathcal{H}_0 t} - i\int_0^t e^{-i\mathcal{H}_0(t-\tau)}[V,\rho(\tau)]\,e^{i\mathcal{H}_0(t-\tau)}\,d\tau$$

Substitution into equ. (37) gives

$$(38) \qquad \dot{\rho} = -i[\mathcal{H}_0,\rho] - i[V,\,e^{-i\mathcal{H}_0 t}\rho_0\,e^{i\mathcal{H}_0 t}]$$
$$- [V,\int_0^t e^{-i\mathcal{H}_0(t-\tau)}[V,\rho(\tau)]\,e^{i\mathcal{H}_0(t-\tau)}\,d\tau]$$

what may be termed the damping form of von Neumann's equation
with an inhomogeneous term, the latter reflecting the non-
commutativity of $\mathcal{H}_0$ and ρ_0 .

The eigenstates $|\alpha\rangle$ of the unperturbed Hamiltonian $\mathcal{H}_0$,
with

$$\mathcal{H}_0 |\alpha\rangle = E_\alpha |\alpha\rangle$$

may form an orthonormal basis of real wave functions
since we shall be not interested in processes involving
dissociation of the molecule. The eigenvalues E_α will be
discrete and there are none but accidental degeneracies.
Denoting

$$\omega_{\alpha\beta} = E_\alpha - E_\beta$$

and changing the integration variable we can write equ. (38)
in matrix form as

$$
(39) \quad
\begin{aligned}
\frac{d\rho_{\alpha\beta}}{dt} = {} & -i\,\omega_{\alpha\beta}\,\rho_{\alpha\beta} - i\sum_\gamma \left\{ V_{\alpha\gamma}\,\rho_{\sigma\gamma\beta}\,e^{-i\omega_{\sigma\gamma}t} - \rho_{\sigma\alpha\gamma}\,V_{\gamma\beta}\,e^{-i\omega_{\alpha\gamma}t} \right\} \\
& -\sum_{\gamma\varepsilon} \left\{ V_{\alpha\gamma}V_{\gamma\varepsilon}\int_0^t e^{-i\omega_{\sigma\gamma}\tau}\rho_{\varepsilon\beta}(t-\tau)\,d\tau - V_{\alpha\gamma}V_{\varepsilon\beta}\int_0^t e^{-i\omega_{\alpha\varepsilon}\tau}\rho_{\gamma\varepsilon}(t-\tau) \right. \\
& \left. - V_{\alpha\gamma}V_{\varepsilon\beta}\int_0^t e^{-i\omega_{\sigma\gamma}\tau}\rho_{\gamma\varepsilon}(t-\tau)\,d\tau + V_{\gamma\varepsilon}V_{\varepsilon\beta}\int_0^t e^{-i\omega_{\alpha\varepsilon}\tau}\rho_{\alpha\gamma}(t-\tau) \right.
\end{aligned}
$$

Equation (39) is nothing but a different form of the von
Neumann equation and therefore still reversible. How-
ever, we expect those terms depending on the square of
the perturbation parameter to turn out as internal inter-
actions ("internal collisions ") of the molecule which
may in some sense give rise to an internal relaxation
process. Even though equ. (39) itself is untreatable we
shall try to construct an asymptotic solution which holds

for the order of magnitude of time which is of physical
interest. To this behalf we first have to study the time-
scales inherent in systems of molecular magnitude.

The asymptotic solution $\rho(t)$ we would like to esta-
blish shall hold for t of the order of the relaxation
time. A necessary condition for such a $\rho(t)$ to exist is[14,15,16]
that two characteristic times of the system ,

14) N.N. Bogoliubov, Studies in Statistical Mechanics,
North-Holland, Amsterdam 1962,p.1.
15) L. Van Hove, La théorie des gaz neutres et ionisés,
Les Houches 1958; Hermann, Paris 1960,p.151.
16) L. Van Hove, Nijenrode castle 1961, p.157.

an atomic time, τ_{at}, and a transversal time, τ_{tr} , are of entire-
ly different orders of magnitude. If our physical interest
in the system, characterized by the expectation values we
want to calculate, requires a time of the order of magnitude
τ_r and

$$(40) \qquad \tau_{at} \ll \tau_r \ll \tau_{tr} \; ,$$

then certain simplifications can be made with equ. (39)
which may allow us to establish the assymptotic form of $\rho(t)$.
In fact, for chemical purposes we shall concentrate on a
time-scale on which mayor changes in nuclear configuration
will take place. Should the system be such that its as-
symptotic behaviour can in some sense be described as a
relaxation process, then τ_r undoubtedly has to be of the order
of the relaxation time.

It is very simple to identify τ_{at} and τ_{tr} for a mole-
cular system. τ_{at} will be the average over the reciprocal
distance between occupied levels,

$$\tau_{at} \simeq \overline{\omega_{\alpha\beta}^{-1}} \; ,$$

whereas τ_{tr} is the average distance between occupied adjacent levels α and α',

$$\tau_{tr} = \overline{\omega_{\alpha\alpha'}^{-1}}$$

Roughly, for molecules undergoing intramolecular conversion, we may put $\overline{\omega_{\alpha\beta}} = E_A$, E_A being the energy difference between the saddle point and the minimum point of the reactant mould on the potential energy surface.

Then, with $E_A \simeq 10^{-1} - 10^{-2}$ at u.,

$$\tau_{at} \simeq E_A^{-1} \simeq 10 - 100 \; at. u \simeq 10^{-16} - 10^{-17} \; sec.$$

Estimation of τ_{tr} requires the knowledge of the density of states in the saddle region. Using the harmonic approximation according to equ. (36) and extending it by assuming

$$\omega_i(\xi) = \omega_i(\xi_{oI}) = \overline{\omega}_i$$

where ξ_{oI} is the minimum of mould I, the condition for a potential curve to have its minimum below energy E_A is

$$(41) \qquad \sum_{i=2}^{M} \overline{\omega}_i n_i \leq E_A - \tfrac{1}{2} \sum_i \overline{\omega}_i$$

The number of sets $\{n_2, \ldots, n_M\}$, fulfilling equ. (41), is approximately (neglecting the zero-point energy in this equation):

$$z(E_A) = \int\limits_{\sum_{k=2}^{M} \overline{\omega}_k n_k \leq E_A} dn_1 dn_2 \cdots dn_M = \frac{1}{\overline{\omega}_2 \, \overline{\omega}_3 \cdots \overline{\omega}_M} \frac{1}{(M-1)!} E_A^{M-1} \; . \qquad 3,17)$$

_____

17) For a more precise estimate see
   E.W. Schlag, R.A. Sandsmark, J.Chem. Phys. **37**, 168 (1962)

Let α be the average density of states in mould I of each of the curves $E_n(\xi)$, Then the density of states $\sigma(E)$ over the saddle region will be

$$\sigma(E_A) = Z(E_A) \cdot \alpha$$

Assuming an average ratio

$$\frac{\overline{E_A}}{\overline{\omega_i}} \simeq 50$$

and a level density

$$\alpha = 10^3 \ (at.u.)^{-1}$$

we have

$$\tau_{tr} \simeq \sigma(E_A)^{-1}$$

and this time will be very large in comparison with τ_{at} and τ_r . For M = 12, 24, 39 we have $\tau_{tr} = 10^{15}$ at.u. (10^{-2}sec), 10^{26} at.u. (10^9sec), 10^{39} at.u. (10^{22} sec) respectively.

These numbers indicate, that condition (40) will be very well fulfilled by molecular systems of chemical significance. It is important to note that even for systems with a small number of degrees of freedom the level density is so high that the uncertainty relation will play a part throughout the process, as the eigenstates of the unperturbed Hamiltonian can never appear separated within times of the order of τ_r . The variation of the matrix elements $\mathcal{L}_{\alpha\beta}$ of an observable $\mathcal{L}$ with α and β , where α is a state out of an energy intervall ΔE_a and β out of ΔE_b, will then be irrelevant if ΔE_a and ΔE_b are of th order τ_r^{-1} or smaller. Therefore we shall find it sufficient to establish an assymptotic solution $\rho(t)_{\alpha\beta}$ of (39)

which also varies slowly with E_α and E_β , the characteristic ranges of change beeing determined by ρ_0 and the matrix elements $V_{\alpha\beta}$. To this end we take several formal steps starting from equ.(39).

The sums in equ.(39) cannot readily be replaced by integrals since the matrix elements $V_{\alpha\beta}$ are not smooth functions of E_α and E_β . However, dividing the energy scale into equal intervals ΔE_1, ΔE_2, ..., ΔE_a, ..., ΔE_b, ... with numbers of states g_1, g_2, ..,g_a, ...,g_b,.... we may average $V_{\alpha\beta}$ over these intervals, writing

$$ V_{\bar{a}\beta} = \frac{1}{g_a} \sum_{\alpha \in a} V_{\alpha\beta} , $$

where $\alpha \in a$ denotes that the states α are taken out of the interval ΔE_a. $V_{\bar{a}\beta}$ will now be a smooth function of the parameter a , if

A1) a large number of states lie in each intervals ΔE_a,

A2) the density of the states $g_a/\Delta E_a$ is a slowly varying function over the energy scale.

In addition , we shall require the length of the interval ΔE, to be of an order of magnitude to fulfill a third condition

A3) $\qquad \Delta E \ll \tau_r^{-1}$

According to A1) every interval will comprise many states of any kind. Following the procedure used in chpt.3 to construct a basis for the molecule with a harmonic approximation one can see that to a given eigenfunction $|\alpha'\rangle$ we may find, within an energy distance of the order of the level splitting, another eigenfunction, $|\alpha''\rangle$, resembling $|\alpha'\rangle$ nearly perfectly,

exept that one oscillator-function contained in $|\alpha''\rangle$ has one
node more whereas another one has one node less. Thus, gi-
ven some $V_{\alpha\beta}$, we may select a large number of matrix ele-
ments with $\alpha \in a$ which differ only slightly from each other.
Since conditions A2) and A3) are easily fulfilled by choos-
ing ΔE_α suitably, the average $V_{\bar{a}\beta}$ may be considered a slow-
ly varying function of $E_{\bar{a}}$

Now we may sum equ. (39) over all $\alpha \in a$ and $\beta \in b$.
Using the notation

$$\sum_{\alpha \in a} \rho_{\alpha\beta} = \rho_{\alpha\beta}$$

$$\frac{1}{g_a g_b} \sum_{\substack{\alpha \in a \\ \beta \in b}} \omega_{\alpha\beta} = \omega_{\bar{a}\bar{b}}$$

we may replace a $\sum_{\gamma}$ by $\sum_{c} g_c$ taken over suitable average
values, ending up with

$$\frac{d\rho_{ab}}{dt} = -i\omega_{\bar{a}\bar{b}}\,\rho_{ab} - i\sum_{c}\left\{ g_a V_{\bar{a}\bar{c}}\,\rho_{ocb}\,e^{-i\omega_{\bar{c}\bar{b}}t} - g_b\,\rho_{oac}V_{\bar{c}\bar{b}}\,e^{-i\omega_{\bar{a}\bar{c}}t}\right\}$$

$$-\sum_{c,e}\left\{ g_a g_c V_{\bar{a}\bar{c}}V_{\bar{c}\bar{e}}\int_0^t e^{-i\omega_{\bar{c}\bar{b}}\tau}\rho_{eb}(t-\tau)d\tau\right.$$

(42)

$$\qquad\qquad - g_a g_b V_{\bar{a}\bar{c}}V_{\bar{e}\bar{b}}\int_0^t e^{-i\omega_{\bar{a}\bar{e}}\tau}\rho_{ce}(t-\tau)\,d\tau$$

$$\qquad - g_a g_b V_{\bar{a}\bar{c}}V_{\bar{e}\bar{b}}\int_0^t e^{-i\omega_{\bar{c}\bar{b}}\tau}\rho_{ce}(t-\tau)\,d\tau$$

$$\qquad\qquad\qquad + g_e g_b V_{\bar{c}\bar{e}}V_{\bar{e}\bar{b}}\int_0^t e^{-i\omega_{\bar{a}\bar{e}}\tau}\rho_{ac}(t-\tau)d\tau \,\cdot$$

Equ. (42), as it stands, may be treated further to find
an asymptotic solution $\rho(t)$. More insight in the nature of
the solution, however, can be gained by the procedure used
in the following.

Since τ_r and τ_{tr}, for most molecular systems, are of such a different magnitude there may be an even coarser contraction over the energy scale for the asymptotic density matrix $\rho(t)$ which nevertheless will lead to the same expectation values. Having choosen a division of the energy scale into intervals ΔE which are as small as possible by order of magnitude, we may find a coarser division into intervals $\Delta E'$, suitable for simplifing the solution of equ. (42) in the following way. Let the intervals be

$$\Delta E_1', \ \Delta E_2', \ \cdots, \ \Delta E_A, \ \cdots, \ \Delta E_B, \ \cdots$$

containing an even larger number of states

$$G_1, \ G_2, \ \cdots, \ G_A, \cdots, \ G_B, \cdots$$

so that

$$G_A = \sum_{\alpha \in A}^{\Box} g_\alpha$$

and

B1) $\quad G_A/g_\alpha \qquad$ is a large number

Furthermore, $\Delta E'$ shall be taken to be as large as possible by order of magnitude, yet fulfilling the requirements

B 2) $\Delta E' \lesssim$ energy interval of characteristic change in $\rho_{\alpha\beta}$ with E_α and E_β (i.e τ_m^{-1})

B 3) $\Delta E' \lesssim$ energy interval of characteristic change of $V_{\bar{a}\bar{b}}$ with $E_{\bar{a}}$ or $E_{\bar{b}}$

B 4) $\Delta E' \ll \tau_r^{-1}$

From the conditions B the requirement B3) will normally be the most restrictive one, thus determining $\Delta E'$. We shall be able to construct an assymptotic density matrix $\rho(t)$, where $\rho_{\alpha\beta}(t)$ will not vary appreciably with $\alpha \in \Delta E_A$ and $\beta \in \Delta E_B$. Our method is somewhat similiar to the use of coarse-grained densities in classical statistical mechanics.[17,18,19]

17) P. Ehrenfest, Collected Scientific Papers, North Holland, Amsterdam, 1959, p. 213

18) D. Ter Haar, Rev. Mod. Phys. 27, 289 (1955)

19) N.G. Van Campen, Nijenrode Castle 1961, p. 173

If we sum equation (42) over $\sum_{\substack{a \in A \\ b \in B}} \sum_{c,e}$ the first two terms on the right hand side can simply be written in terms of the indices A,B,C, whereas the collision terms can be given further treatment. Let us look in detail at the first collision integral; the others can be handled in analogous way:

$$
(43) \quad
\begin{aligned}
&\sum_{\substack{a \in A \\ b \in B}} \sum_{c,e} g_a g_c V_{\bar{a}\bar{c}} V_{\bar{c}\bar{e}} \int_0^t e^{-i\omega_{\bar{c}\bar{b}}\tau} \rho_{eb}(t-\tau)\,d\tau = \\
&= \sum_{c,e} G_A g_c V_{\bar{A}\bar{c}} V_{\bar{c}\bar{e}} \frac{G_B}{\Delta E' g_{\bar{B}}} \int_0^t \frac{e^{-i\omega_{\bar{c}B+1}\tau} - e^{-i\omega_{\bar{c}B}\tau}}{i\tau} \rho_{eb}(t-\tau)\,d\tau .
\end{aligned}
$$

Expanding $\rho(t-\tau)$ under the integral-sign in a Taylor-series

$$
\rho(t-\tau) = \sum_{k=1}^{\infty} \frac{(-\tau)^k}{k!} \rho^{(k)}(t)
$$

we have to evaluate the integrals

$$
(44) \quad \mathcal{J}_k = \int_0^t \frac{(-\tau)^k}{k!} \frac{e^{-i\omega_{\bar{c}B+1}\tau} - e^{-i\omega_{\bar{c}B}\tau}}{i\tau}\,d\tau .
$$

The $\mathcal{F}_k$ can be generated out of each other by differentiation.

$$\mathcal{F}_k = \frac{1}{i^k k!} \frac{\partial^k}{\partial \omega^k} \mathcal{F}_0$$

Since $\omega_{\zeta B} t \gg 1$ for nearly all terms under the sum in (43) it can be readily seen (introducing $\tau' = \omega_{\zeta B} \tau$ as a new variable of integration) that the upper limit in the integral (44) may be taken infinite. Then we have

$$\mathcal{R}e \; \mathcal{F}_0 = \Theta_B (E_{\zeta}) \quad \text{where} \quad \Theta_B(E_{\zeta}) = \begin{cases} 0 & \text{for } E_{\zeta} \; \begin{matrix} > E_{B+1} \\ < E_B \end{matrix} \\ \pi & \text{''} \quad E_B < E_{\zeta} < E_{B+1} \end{cases}$$

$$\mathcal{I}m \; \mathcal{F}_0 = i \, \Delta E' \, \mathcal{P}(\frac{1}{\omega_{\zeta B}}),$$

$\mathcal{P}$ denoting the principal value,

or

(45) $\qquad \mathcal{F}_0 = \Theta_B (E_{\zeta}) + i \, \Delta E' \, \mathcal{P}(\frac{1}{\omega_{\zeta B}})$

Furthermore

$$\mathcal{F}_1 = 2\pi i \left(\delta_+ (\omega_{\zeta B+1}) - \delta_+ (\omega_{\zeta B}) \right)$$

and

$$\mathcal{F}_k = -\frac{2\pi}{i^k k!} \frac{\partial^{k-1}}{\partial \omega^{k-1}} \left(\delta_+ (\omega_{\zeta B+1}) - \delta_+ (\omega_{\zeta B}) \right)$$

$$= -\frac{2\pi}{i^k k!} \left(\delta_+^{(k-1)} (\omega_{\zeta B+1}) - \delta_+^{(k-1)} (\omega_{\zeta B}) \right)$$

$\delta_+ (\omega)$ can also be represented by

(46) $\qquad \delta_+ (\omega) = \lim_{\varepsilon \to 0} \frac{1}{2\pi i} \cdot \frac{1}{\omega - i\varepsilon} \quad .$

and therefore

$$(47) \qquad \delta_+^{(k-1)}(\omega) = \frac{(-1)^{k-1}(k-1)!}{2\pi i} \lim_{\varepsilon \to 0} \frac{1}{(\omega - i\varepsilon)^k}$$

The collison term (43) can now be written as follows:

$$\sum_{k=0}^{\infty} \sum_{c,e} \frac{G_A G_B}{\Delta E' g_{\bar{B}}} g_c V_{\bar{A}\bar{c}} V_{\bar{c}\bar{e}} \, \rho_{eb}^{(k)}(t) \, \mathcal{F}_k(\omega_{\bar{c}B+1}, \omega_{\bar{c}B})$$

$$(48) \qquad = \sum_{k=0}^{\infty} \frac{G_A G_B}{\Delta E' g_{\bar{B}}} \int_0^{\infty} dE_{\bar{c}} \, dE_{\bar{e}} \, g(E_c) V(E_{\bar{A}}, E_{\bar{c}}) V(E_{\bar{c}}, E_{\bar{e}}) \rho^{(k)}(E_{\bar{e}}, E_{\bar{b}}; t) \mathcal{F}_k$$

$$= \sum_{k=0}^{\infty} \frac{G_A G_B}{\Delta E' g_{\bar{B}}} \int_0^{\infty} dE_{\bar{e}} \int_{-E_B}^{\infty} d\omega \, g(E_B + \omega) V(E_{\bar{A}}, E_B + \omega) V(E_B + \omega, E_{\bar{e}}) \rho^{(k)}(E_{\bar{e}}, E_{\bar{b}}; t) \mathcal{F}_k(\omega)$$

where $\omega = E_{\bar{c}} - E_B$ was introduced as new integration variable.

We can now show that the ratio of two consecutive terms of the k-sum in (48) will be small.
The ω - integral in (48) has the general form

$$(49) \qquad C_k = \int_{-E_B}^{\infty} d\omega \, F(\omega) \, \mathcal{F}_k(\omega + \Delta E', \omega)$$

Where $F(\omega)$ is slowly varying with ω. It is easy to see that the ratio between the terms with k=1 and k=0 is small. We have

$$C_0 = \int_{-E_B}^{\infty} d\omega \, F(\omega) \, \mathcal{F}_0(\omega + \Delta E', \omega) = \int_{-E_B}^{\infty} d\omega \, F(\omega) \, \Delta E' 2\pi \, \delta_+(\omega)$$

$$C_1 = \int_{-E_B}^{\infty} d\omega \, F(\omega) \, \mathcal{F}_1(\omega + \Delta E', \omega) = \int_{-E_B}^{\infty} d\omega \, F(\omega) \, 2\pi i (\delta_+(\omega + \Delta E') - \delta_+(\omega))$$

$F(\omega)$ can be extended analytically outside the real axis. Since it is proportional to transition matrix elements V_{ab} we may also assume that $F(\omega)$ vanishes sufficiently strong at the infinite point. Furthermore, E_B is so large compared with $\Delta E'$ that the lower limit in (49) can be replaced by ∞. Then, by (46) and

$$\int_{-E_B}^{\infty} \cdots d\omega = \int_{\mathcal{O}} \cdots d\omega ,$$

the integration taken along $-\infty$ to $+\infty$ and encircling the positive imaginary halfplane, we have

$$\frac{\rho'(t) c_1}{\rho(t) c_0} \simeq \frac{\rho/\tau_r \left(F(-\Delta E') - F(0) \right)}{\rho \cdot \Delta E' \cdot F(0)} \simeq \frac{1}{\tau_r} \frac{F'(0)}{F(0)} \simeq \frac{F(0)/E_A}{\tau_r F(0)} = \frac{\tau_a}{\tau_r} \ll 1$$

Similarly, we find by (47)

$$\frac{\rho^{(k)}(t) c_k}{\rho^{(k-1)}(t) c_{k-1}} \simeq \frac{\rho^{(k-1)}/\tau_r \cdot \left(F^{(k-1)}(-\Delta E') - F^{(k-1)}(0) \right)}{\rho^{(k-1)} \left(F^{(k-2)}(-\Delta E') - F^{(k-2)}(0) \right)} \simeq \frac{1}{\tau_r} \frac{F^{(k)}(0)}{F^{(k-1)}(0)}$$

$$\simeq \frac{\tau_{at} F^{(k-1)}(0)}{\tau_r F^{(k-1)}(0)} = \frac{\tau_{at}}{\tau_r} \ll 1$$

$\rho^{(k)}(t) \simeq \rho^{(k-1)}(t) \cdot \tau_r^{-1}$ and $F^{(k)}(0) = F^{(k-1)}(0) E_A^{-1} = F^{(k-1)}(0) \cdot \tau_a$ follows

from the previous assumptions that these functions are

expandable in power series which decline rapidly outside the
circles of radius $\mathcal{T}_r$ and E_A respectively.

Our system is thus big enough to neglect higher order
terms in the expansion of ρ $(t - \mathcal{T})$ (for infinite systems
see E. Montrolls[13] treatment). These achievements shall
allow us to rewrite equ. (42) for an assymptotic density
matrix, defined over the coarser energy scale $\Delta E'$.
Since all functions occuring in the collision terms are smooth
enough, $\mathcal{J}_o$ from equ. (42) may be replaced by

$$\mathcal{J}_o = \Delta E' \, 2\pi \, d_+ (\omega_{\bar{C}B}).$$

The imaginary part of $d_+(\omega_{\bar{C}B})$ will give rise to a renormali-
zation of the energy levels which has little effect on the
assymptotic solution. We shall, for the sake of simplicity,
leave out the principal value integral replacing $d_+(\omega)$ by
$\frac{1}{2} d(\omega)$. We then end up with

$$\frac{d \rho_{AB}}{dt} = -i\omega_{A\bar{B}} \, \rho_{AB} - i \sum_{C}' \left\{ G_A V_{A\bar{C}} \rho_{o\bar{C}B} e^{-i\omega_{\bar{C}B}t} - G_B \rho_{o AC} V_{\bar{C}\bar{B}} e^{-i\omega_{A\bar{C}}t} \right\}$$

$$(50) \qquad -\pi \sum_{C,E}' G_A G_B \left\{ V_{A\bar{C}} V_{\bar{C}E} \rho_{EB} \, d_{\bar{C}B} - V_{A\bar{C}} V_{E\bar{B}} \rho_{CE} \, d_{AE} \right.$$

$$\left. - V_{A\bar{C}} V_{E\bar{B}} \rho_{CE} \, d_{CB} + V_{\bar{C}E} V_{E\bar{B}} \rho_{AC} \, d_{AE} \right\} \Big)$$

where the $d's$ represent ordinary Kronecker symbols. Equ.(50)
is a master equation with an inhomogeneous term.

It may be worth noting that for the derivation of a master equation the coarser energy scale $\Delta E'$ is not an essential step. The derivation given here yet has the advantage of simplifying the interpretation of dispersion integrals as δ_+-functions what is not quite so trivial after the first coarse-graining step.

Equ. (50) can in turn be written in terms of the original basis $\{|\alpha\rangle\}$ and generalized to an operator equation

$$(51) \qquad \frac{d\varrho}{dt} = -i[\mathcal{H}_0, \varrho] - \pi[\bar{V}, [\bar{V}, \varrho]_{(d)}] - i[\bar{U}, e^{-i\mathcal{H}_0 t}\varrho_0 e^{i\mathcal{H}_0 t}],$$

where $[\bar{V}, \varrho]_{(d)}$ denotes the diagonal part of the commutator $[\bar{V}, \varrho]$, and $\bar{U}$ is an operator the matrix elements of which are smooth functions over the energy scale, the characteristic energy interval for a change of $\bar{V}_{\alpha\beta}$ being $\Delta E'$. $\bar{U}$ may be defined as

$$\bar{U} = \sum_{\alpha, \beta}{}' |\alpha\rangle \bar{V}_{\alpha\beta} \langle\beta|$$

$$(52) \qquad\qquad = \sum_{A, B}{}' \sum_{\substack{\alpha \in A \\ \beta \in B}} |\alpha\rangle V_{\bar{A}\bar{B}} \langle\beta|$$

Note that $\bar{V}_{\alpha\beta}$ is a real symmetric matrix, just like $V_{\alpha\beta}$ itself, since the basis we are using contains real bound functions only.

4) The Character of the Solutions

Equ. (51), by virtue of its inhomogeneous term, may have so-
lutions which behave oscillatory at infinite times. It is there-
fore necessary to prove that a relaxating assymptotic solution
$\rho(t)$ exists which fulfills the requirements A and B stated in
chpt. 3. As main reason for a relaxating $\rho(t)$ to exist we shall
find the smoothness of ρ_o over the energy scale, with other words,
the condition that the time τ_m, allowed for preparation of the
initial state, has to be such that $\tau_m \ll \tau_r$. If we could prepare
initial states in an arbitraty way we might well be able to choose
ρ_o such that the assymtotic $\rho(t)$ remains oscillatory.

The homogeneous part of equ. (51) has to be treated first.
To that behalf we have to investigate the underlying eigenvalue
problem,

$$(53) \qquad \mathcal{L} \rho^{(q)} \equiv -i [\mathcal{H}_o, \rho^{(q)}] - \kappa [\bar{V}, [\bar{V}, \rho^{(q)}]_{(\alpha)}] = \lambda_q \rho^{(q)}$$

This operator equation may now be turned into a matrix equation
by introducing a basis $\{|\alpha\rangle\}$. Considering the smoothness of $\bar{V}_{\alpha\beta}$
over energy intervals $\Delta E'$ one should keep in mind that the ei-
genvalue-problem (53) over the basis $\{|\alpha\rangle\}$ can readily be con-
tracted in the same way as equ (39) was summed and smoothed
over all $\alpha \in a$ and $\beta \in b$, respectively all $a \in A$ and $b \in B$. The
basis $\{|\alpha\rangle\}$ is used here for simplicity of writing only. $\{|\alpha\rangle\}$
may be truncated to a finite set by eliminating all $|\alpha\rangle$ with
$E_\alpha > E_{max}$, where E_{max} is an energy above which the occupation
density of the levels is negligibly small.

Equ. (53) can then be solved within the linear vector space
of n-th order square matrices over the field of complex numbers.

In that case we have to define the inner product as

$$\left(\rho^{(1)}, \rho^{(2)} \right) = \sum_{\alpha,\beta} \rho^{(1)*}_{\alpha\beta} \, \rho^{(2)}_{\alpha\beta}$$

and assume the $\rho^{(q)}$ to be normalised so that

$$\left(\rho^{(q)}, \rho^{(q)} \right) = 1$$

Now we can show the following:

T1)   Symmetric eigenmatrices of equ. (53) belong to zero eigen-
values and are diagonal.

Let $\rho^{(\tilde{q})}$ be any symmetric eigenmatrix, then the collision
term will be zero, since $\mathcal{V}$ is symmetric and therefore
$[\bar{\mathcal{V}}, \rho^{(\tilde{q})}]_{(k)} = 0$. From the quadratic form of $\mathcal{L}$ remains only

$$-i \left(\rho^{(\tilde{q})}, [\mathcal{H}_0, \rho^{(\tilde{q})}] \right) = \lambda_{\tilde{q}}$$

or

$$\lambda_{\tilde{q}} = -i \sum_{\alpha\beta} \rho^{(\tilde{q})*}_{\alpha\beta} [\mathcal{H}_0, \rho^{(\tilde{q})}]_{\alpha\beta} = -i \sum_{\alpha\beta} \omega_{\alpha\beta} \, |\rho^{(\tilde{q})}_{\alpha\beta}|^2 = 0,$$

since the sum changes sign when interchanging α and β.

Furthermore, from

$$-i [\mathcal{H}_0, \rho^{(\tilde{q})}] = 0$$

or

$$-i \omega_{\alpha\beta} \, \rho^{(\tilde{q})}_{\alpha\beta} = 0$$

follows

$$\rho^{(\tilde{q})}_{\alpha\beta} = 0 \qquad \text{for } \alpha \neq \beta$$

T2)   If all $\bar{V}_{\alpha\beta} \neq 0$ the nonvanishing eigenvalues have a nega-
tive real part.

$\rho^{(\hat{q})}$ shall denote a non-symmetric eigenmatrix. Then

$$\left(\rho^{(\hat{q})}, \mathscr{L}\,\rho^{(\hat{q})}\right) = -i\left(\rho^{(\hat{q})}, \left[\mathcal{H}_0, \rho^{(\hat{q})}\right]\right) - \pi\left(\rho^{(\hat{q})}, \left[\bar{V}, \left[\bar{V}, \rho^{(\hat{q})}\right]_{(d)}\right]\right)$$

$$= -i\sum_{\alpha\beta}\rho^{(\hat{q})*}_{\alpha\beta}\left[\mathcal{H}_0, \rho^{(\hat{q})}\right]_{\alpha\beta} - \pi\sum_{\alpha\beta}\rho^{(\hat{q})*}_{\alpha\beta}\,\bar{V}_{\alpha\beta}\left\{\left[\bar{V}, \rho^{(\hat{q})}\right]_{\beta\beta} - \left[\bar{V}, \rho^{(\hat{q})}\right]_{\alpha\alpha}\right\}$$

$$= -i\sum_{\alpha\beta}\omega_{\alpha\beta}\,\rho^{(\hat{q})*}_{\alpha\beta}\,\rho^{(\hat{q})}_{\alpha\beta} - \pi\sum_{\alpha}\left[\rho^{(\hat{q})+}, \bar{V}\right]_{\alpha\alpha}\left[\bar{V}, \rho^{(\hat{q})}\right]_{\alpha\alpha}$$

$$= -i\sum_{\alpha\beta}\omega_{\alpha\beta}\left|\rho^{(\hat{q})}_{\alpha\beta}\right|^2 - \pi\sum_{\alpha}\left|\left[\bar{V}, \rho^{(\hat{q})}\right]_{\alpha\alpha}\right|^2 = \lambda_{\hat{q}},$$

thus $\mathrm{Re}\,\lambda_{\hat{q}} < 0$.

The condition $\bar{V}_{\alpha\beta} \neq 0$ for all α and β is not a very strong one since $\bar{V}$ is an average over a large number of states. Even if many of the $V_{\alpha\beta}$ should be exactly zero by symmetry requirements $\bar{V}_{\alpha\beta}$ would be different from zero.

By means of T1 and T2 it is also easy to see that the eigenvalues $\lambda_{\hat{q}}$, belonging to non-diagonal eigen-matrices, are non-degenerate and that any two such $\rho^{(\hat{q})}$ are linearly independent.

The homogeneous equation (51) will then have the solution

$$(54) \qquad \rho_h(t) = \sum_{q}{}' \rho^{(q)}\,d_q\,e^{\lambda_q t}$$

where the d_q, are uniquely determined by ρ_0, namely

$$\rho_0 = \sum_{q}{}' \rho^{(q)}\,d_q.$$

We shall first look at the diagonal part of $\rho(t)$. In this case only the inhomogeneous term may play any role:

$$\frac{d\rho_{\alpha\alpha}}{dt} = -i\left[\bar{V}, e^{-i\mathcal{H}_0 t}\rho_0 e^{i\mathcal{H}_0 t}\right]_{\alpha\alpha}$$

$$= \sum_{\gamma}\bar{V}_{\alpha\gamma}\left(\rho_{0\gamma\alpha}e^{-i\omega_{\gamma\alpha}t} - \rho_{0\alpha\gamma}e^{-i\omega_{\alpha\gamma}t}\right)$$

The γ-sum can be converted into an integral readily. ρ_0 is a real, symmetric matrix, therefore

$$(55) \qquad \rho_{\alpha\alpha}(t) - \rho_{0\alpha\alpha} = 2\pi\sum_{\gamma}\bar{V}_{\alpha\gamma}\left(\rho_{0\gamma\alpha}\delta_+(\omega_{\gamma\alpha}) - \rho_{0\alpha\gamma}\delta_+(\omega_{\alpha\gamma})\right)$$

$$= 0.$$

As one might have expected beforehand the occupation of the eigenstates of $\mathcal{H}_0$ in the ensemble does not change in time since there are no external collisions and we are dealing with the time-assymptote of the density matrix.

For obtaining the solution of the inhomogeneous equation we have to expand the inhomogeneous part in terms of the eigen-matrices $\rho^{(q)}$. As the diagonal part of the inhomogeneous term contributes only to the constant $\rho_{0\alpha\alpha}$, we can confine ourselves to expanding the non-diagonal part of this term, thus having non-symmetric matrices in the expansion:

$$(56) \qquad -i\left[\bar{V}, e^{-i\mathcal{H}_0 t}\rho_0 e^{i\mathcal{H}_0 t}\right] = \sum_{\hat{q}}\rho^{(\hat{q})}f_{\hat{q}}(t)$$

The general form of $f_{\hat{q}}(t)$ needs to be worked out for later con-clusions. Using the linear independence of the $\rho^{(q)}$ we can form the inner product of equ.(56) with $\rho^{(\hat{r})}$:

$$\sum_{\hat{q}} (\rho^{(\hat{r})}, \rho^{(\hat{q})}) f_{\hat{q}}(t) = -i \sum_{\alpha\beta\gamma} \rho^{(\hat{r})*}_{\alpha\beta} \left(\bar{V}_{\alpha\gamma} \rho_{o\gamma\beta} e^{-i\omega_{\gamma\beta}t} - \rho_{o\alpha\gamma} \bar{V}_{\gamma\beta} e^{-i\omega_{\alpha\gamma}t} \right)$$

$$= -i \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \rho_{o\gamma\beta} \sum_{\alpha} \rho^{(\hat{r})*}_{\alpha\beta} \left(\bar{V}_{\alpha\gamma} - \bar{V}_{\beta\alpha} \right)$$

(57)
$$= -i \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} R^{(\hat{r})}_{\beta\gamma} \,,$$

(57a)
$$R^{(\hat{r})}_{\beta\gamma} = \rho_{o\alpha\beta} \sum_{\alpha} \rho^{(\hat{r})*}_{\alpha\beta} \left(\bar{V}_{\alpha\gamma} - \bar{V}_{\beta\alpha} \right).$$

Denoting

$$D = det(\rho^{(\hat{r})}, \rho^{(\hat{q})})$$

and the adjoint determinant of D by $D^{\hat{q},\hat{r}}$, we can obtain $f_{\hat{q}}(t)$ from equ.(57) by

$$f_{\hat{q}}(t) = -\frac{i}{D} \sum_{\hat{r}} D^{\hat{r},\hat{q}} \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} R^{(\hat{r})}_{\beta\gamma}$$

(58)
$$= \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \left(\frac{-i}{D} \sum_{\hat{r}} D^{\hat{r}\hat{q}} R^{(\hat{r})}_{\beta\gamma} \right)$$

$$= \sum_{\beta\gamma} e^{-i\omega_{\gamma\beta}t} \cdot Q^{(\hat{q})}_{\beta\gamma}$$

We can easily see now that $Q^{(\hat{q})}_{\beta\gamma}$ is a smooth function of E_β and E_γ . This will be so if $R^{(\rho)}_{\beta\gamma}$ is a smooth function of these variables. By (57a) we can see that $R^{(\hat{r})}_{\beta\gamma}$ depends in a smooth way on E_γ only if $\rho^{(\hat{r})}_{\alpha\beta}$ depends smoothly on E_β . This can be seen by looking at equ.(52) for the eigenvector $\rho^{(\hat{r})\dagger}$, belonging to an eigenvalue $\lambda^*_{\hat{q}}$ and forming the $\beta\alpha$ -matrix elements:

$$-i\omega_{\beta\alpha} \rho^{(\hat{r})*}_{\alpha\beta} - \varkappa \sum_{\gamma} \bar{V}_{\beta\alpha} \bar{V}_{\alpha\gamma} \left(\rho^{(\hat{r})*}_{\alpha\gamma} - \rho^{(\hat{r})*}_{\gamma\alpha} \right) = \lambda^*_{\hat{q}} \rho^{(\hat{r})*}_{\alpha\beta}$$

or

$$\rho^{(\hat{r})}_{\alpha\beta} = \frac{\pi}{i\omega_{\alpha\beta}+\lambda_{\hat{q}}} \sum_{\gamma} \bar{V}_{\beta\alpha}\bar{V}_{\alpha\gamma}\left(\rho^{(\hat{r})}_{\alpha\gamma} - \rho^{(\hat{r})}_{\gamma\alpha}\right)$$

Therefore $\rho^{(\hat{r})}_{\alpha\beta}$ depends on E_β as smooth as $\bar{V}_{\beta\alpha}/(i\omega_{\alpha\beta}+\lambda_{\hat{q}})$, what is perfectly sufficient to convert the γ-sum in (58) into an integral.

The total solution of equ. (51) then has the form

$$\rho(t) = \sum_{q} \rho^{(q)} d_q e^{\lambda_q t} + \sum_{\hat{q}} \rho^{(\hat{q})} e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}}\tau} f_{\hat{q}}(\tau)d\tau$$

(58)

$$= \rho_{o(d)} + \sum_{\hat{q}} \rho^{(\hat{q})} d_{\hat{q}} e^{\lambda_{\hat{q}} t} + \sum_{\hat{q}} \rho^{(\hat{q})} e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}}\tau} f_{\hat{q}}(\tau)d\tau$$

where $\rho_{o(d)}$ is the diagonal matrix representing the diagonal part of ρ_o. According to T1 all $\lambda_{\hat{q}}$ have a non-vanishing$_\lambda$ $\overset{negative}{}$ real part, therefore the terms under the first sum are damped exponentially, but this is not immediately clear for the terms under the second sum of equ. (58). We have

$$e^{\lambda_{\hat{q}} t} \int_0^t e^{-\lambda_{\hat{q}}\tau} f_{\hat{q}}(\tau)d\tau = \sum_{\beta\gamma} e^{\lambda_q t} Q^{(\hat{q})}_{\beta\gamma} \int_0^t e^{(-i\omega_{\gamma\beta}-\lambda_q)\tau}d\tau$$

(59)

$$= \sum_{\beta\gamma} \frac{e^{-i\omega_{\gamma\beta}t}-e^{\lambda_{\hat{q}}t}}{-i\omega_{\gamma\beta}-\lambda_{\hat{q}}} Q^{(\hat{q})}_{\beta\gamma}$$

The second term under the sum is again damped, so we focus attention on the first:

$$\sum_{\beta\gamma}{}' \frac{e^{-i\omega_{\gamma\beta}t}}{-i\omega_{\gamma\beta}-\lambda_{\hat{q}}} Q^{(\hat{q})}_{\beta\gamma} = \int_0^\infty dE_\gamma\, dE_\beta\, \sigma(E_\beta)\,\sigma(E_\gamma)\, \frac{e^{-i\omega_{\gamma\beta}t}}{-i\omega_{\gamma\beta}-\lambda_{\hat{q}}} \cdot Q^{(\hat{q})}(E_\beta, E_\gamma)$$

where $\sigma(E)$ is the density of states. By the substitution

$$E_\beta = E$$
$$E_\gamma = \frac{z}{t} + i\lambda_{\hat{q}} + E$$

this goes over into

$$e^{\lambda_{\hat{q}}t}\int_0^\infty dE\,\sigma(E)\int_{-(E+i\lambda_{\hat{q}})t}^{\infty-i\lambda_{\hat{q}}t} \sigma\!\left(\frac{z}{t}+E+i\lambda_{\hat{q}}\right) Q^{(\hat{q})}\!\left(E,\frac{z}{t}+E+i\lambda_{\hat{q}}\right)\frac{e^{-iz}}{-iz}\,dz$$

The integration path of the inner integral is from the point $-(E+i\lambda_{\hat{q}})t$, which is lying in the positiv half-plane, parallel to the real axis to $+\infty$. The distance of the integration path from the real axis is of the order of magnitude 1, since

$$t \simeq \tau_\gamma \simeq \overline{Re\,\lambda_{\hat{q}}}^{\,-1}$$

We then extend the integrand analytically and close the integral path C by encircling the negative imaginary half-plane clockwise, coming back to the point $-(E+i\lambda_{\hat{q}})t$ which is of the order infinity under the outer integral. We obtain

$$e^{\lambda_{\hat{q}}t}\int_0^\infty dE\,\sigma(E)\int_C \sigma\!\left(\frac{z}{t}+E+i\lambda_{\hat{q}}\right) Q^{(\hat{q})}\!\left(E,\frac{z}{t}+E+i\lambda_{\hat{q}}\right)\frac{e^{-iz}}{-iz}\,dz$$

$$= i\,e^{\lambda_{\hat{q}}t}\int_0^\infty dE\,\sigma(E)\,\sigma(E+i\lambda_{\hat{q}})\,Q^{(\hat{q})}(E,E+i\lambda_{\hat{q}})$$

This shows that the terms in the second sum of (58) are indeed damped exponentially.

5) Conclusion

We were able to derive a master equation for an ensemble of isolated molecules. It should be borne in mind, however, that the statement of equilibrium for the molecular system by some kind of experiment is bound to a time scale τ_{eq} of the order

$$\tau_{eq} \ll \tau_{tr}$$

the necessary requirements were of a rather general nature and likely to be fulfilled for molecules with 6 or more atoms. inequality (40) will always hold if $\overline{V}$ is sufficiently small, as can easily be seen by equs. (54) and (41a). Furthermore, the smoothness of $V_{\alpha\beta}$, guaranteed by conditions A1)-A3), can hardly be thought to be not fulfilled in any non-pathological case. it was mentioned before that the requirements B1)-B4) are not essential in deriving the master equation they may, however, in practice play an important role for condensing the original set of equations to a lower order. in many instances condensation may be possible to an extent where the range of energy involved is divided into 10 intervals only and yet allows to describe the relaxation process with sufficient accuracy. Estimation of such very coarse matrix-elements V_{AB}, partly by experiment, is then not inconcivable any more.

A crude way of determining by order of magnitude the rate of an intramolecular rearrangement reaction (in the region where it is of first order) would be to use a suitable average over the $Re\,\lambda_q$ as a rate coefficient. Determining τ_r such that

$$\sum_{q} e^{Re\,\lambda_q \cdot \tau_r} = 1$$

we could use

$$\bar{k} \simeq \frac{1}{\tau_r}$$

as a rate coefficient.

According to the outline in chpt.2 the complete expression for the rate will be

$$R = \frac{d}{dt} tr(\mathcal{K}^{\overline{II}} \rho) = tr\left(\mathcal{K}^{II} \frac{d\rho}{dt}\right)$$

The general form of $\rho(t)$ is

$$\rho(t) = \rho_{o(d)} + \sum_{\hat{q}} \rho^{(\hat{q})} e^{\lambda_{\hat{q}} t} F_{\hat{q}}$$

and

$$\frac{d\rho}{dt} = \sum_{\hat{q}} \rho^{(\hat{q})} \lambda_{\hat{q}} e^{\lambda_{\hat{q}} t} F_{\hat{q}}$$

so that

(60)
$$R = \sum_{\hat{q}} \lambda_{\hat{q}} e^{\lambda_{\hat{q}} t} F_{\hat{q}} tr(\mathcal{K}^{II} \rho^{(\hat{q})})$$

R by equ. (60) is a real quantity because the eigenvalues appear pairwise, i.e. if $\lambda_{\hat{q}}$ is an eigenvalue $\lambda_{\hat{q}}^{*}$ is also one.

Finally we may study the mechanism in an intramolecular conversion reaction including vibrational relaxation after external collisions. Though we did not include external collisions explicitely in the description of the relaxation process we can make use of the master equation (51) for the period between collisions. If the duration of an external collision is short compared with the time between collisions, τ_{coll}, we may again specify an initial density ρ_o^I by a set

of commuting observables. ρ_o^I is then the initial state of
an ensemble representing wave packets which are localized onto
configuration I. Applying equ. (51) we can say the following:
ρ_o^I will, in an eigenrepresentation of $\mathcal{H}_o$, have large ele-
ments far from the diagonal. In the expansion of ρ_o^I in terms
of the eigenmatrices $\rho^{(q)}$,

$$\rho_o^I = \sum_q{}' \rho^{(q)} d_q^I \, ,$$

there will large d_q^I occur for highly unsymmetric $\rho^{(q)}$.
By equation (54), the negative real parts of the eigenvalues
corresponding to these eigenmatrices are the largest. Thus,
the parts of the density matrix far from the diagonal will
quickly be damped away. We arrive at the same result if we
set up equ. (51) for a density matrix $\rho^I(t)$ with $\mathcal{H}_o^I$ instead
of $\mathcal{H}_o$. From the latter case we can see immediately that

$$\lim_{t \to \infty} \rho^I(t) = \rho_o \, ,$$

ρ_o being the one defined in chpt.2 and the relaxation time
τ_r^I for this process may be used to determine the order of
the observation time τ_m, for identifying the initial state
of the species I,

$$\tau_m \simeq \tau_r^I$$

Thus, if $\tau_r^I \ll \tau_{coll}$ and τ_r, what will usually be the case,
and also the characteristic change of the diagonal elements
of ρ by the external collisions is slow compared with τ_r,
equ.(51) will give the correct rate for the isomerization
reaction.

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